(12) UK Patent Application (19) GB (11) 2 045 829 A

(21) Application No 8009684
(22) Date of filing 21 Mar 1980
(30) Priority data
(31) 7907247
(32) 22 Mar 1979
(33) France (FR)
(43) Application published
5 Nov 1980
(51) INT CL³
D21H 5/20
D04H 1/58
(52) Domestic classification
D2B 11B2 11B3 11B4
11BY 11C1 11CY 11E 15 1
20 36D1 36M2 36M3
36MY 36Q1 36Q2 36Q5
36QY 36S 41A 7
(56) Documents cited
GB 1513712
GB 1321428
GB 1017023
GB 572962
GB 569738
GB 301428
(58) Field of search
D2B
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(54) **Leather fibre-containing compound material and process for manufacturing the same**

(57) A compound material contains, by weight, x% leather fibres, y% fibrillar or/and powdery polymeric thermoplastic binder and z% reinforcing fibres, x, y and z being so selected that $30 \leq x \leq 80$, $20 \leq y \leq 70$ and $5 \leq z \leq 25$, where $x+y+z = 100$. The fibres of the compound material are bonded to each other at their points of contact by means of the binder. This novel material is useful in the fancy-leather goods and boot and shoe industries.

The binder has a softening point below 180°C, and is a polymer or copolymer of an olefine or a vinyl or acrylic monomer, a polyamide, a polyester or a polycarbonate or mixture of these.

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SPECIFICATION

Leather fibre-containing compound material and process for manufacturing the same

The present invention is related to a leatherette material containing leather fibres. "Leatherette" is also known as "artificial leather" or "imitation leather". The invention also concerns a process of manufacturing this material, as well as uses thereof, especially in the boot and shoe manufacturing and fancy leather goods industries.

In known kinds of leatherette manufactured by conventional processes the leather fibres are bonded by means of chemical binders which are generally applied in the form of emulsions. These known leatherette materials exhibit comparatively poor mechanical properties, due to the reduced length of the leather fibres. Furthermore these conventional leatherette materials show rather poor hygienic properties, such as water vapour absorption and desorption, due to the fact that the leather fibres are coated with emulsionized binder.

In the field of boot and shoe manufacturing, especially in the so-called "first sole" manufacture, it has been proposed to use materials prepared from cellulose fibres and chemical binders in the form of emulsions. Although these cellulose-based materials exhibit improved mechanical properties, their hygienic properties are less satisfactory.

It is an object of the present invention to provide a novel leather fibre-containing compound material which, on the one hand, exhibits mechanical properties at least equivalent to those of the cellulose-based fibres and, on the other hand, shows hygienic properties substantially more satisfactory than those of said cellulose-based materials or those of conventional leatherette materials.

Such novel compound material is obtained, on the one hand, by replacing the conventional chemical binder, which entirely covers the leather or cellulose fibres, by a fibrillar or/and powdery thermoplastic polymeric binder which forms bonds at the locations of crossing or entangling of the fibres and, on the other hand, by associating the leather fibres with a certain proportion of reinforcing fibres. Owing to this arrangement, the hydrophilic properties of the leather fibres incorporated in the compound material are retained, while the mechanical properties of said material - particularly the flexional strength, the tearing strength and the moist abrasion strength - are substantially improved.

The compound material according to the invention contains, by weight, x% leather fibres, y% fibrillar or/and powdery thermoplastic polymeric binder and z% reinforcing fibres, the respective values of x, y and z being so selected that $30 \leq x \leq 80$, $20 \leq y \leq 70$ and $5 \leq z \leq 25$, $x+y+z$ being equal to 100, said fibres being mutually bonded at a plurality of respective points thereof by said thermoplastic binder.

The leather fibres used for preparing said compound material have a length generally from 0.2 to 5 millimeters, preferably 0.5 to 3 millimeters. These fibres may be produced by defibrillation of waste leather, by wet refining or by dry crushing.

In the present description the expression "fibrillar or/and powdery thermoplastic polymeric binder" is used to designate a thermoplastic polymeric binder in the form of fibrils (fibrillae) (fibrillar binder) or in the form of a powder (powderous binder), wherein the thermoplastic polymer concerned has a softening point of less than 180°C and is selected from the group consisting in polyolefins, especially polyethylene, crystalline olefin copolymers, preferably ethylene/propylene or propylene/butene block copolymers, crystalline olefin and vinyl monomer copolymers, preferably crystalline ethylene and vinyl acetate copolymers, crystalline ethylene and alkyl acrylate or methacrylate copolymers, mixtures of polyolefins or/and olefin copolymers of the above-indicated types, polyamides or copolyamides, polyesters, polycarbonates, acrylic polymers and vinyl polymers. Advantageously the thermoplastic polymer used as a binder is constituted by a polymer of copolymer, or a polymer or/and copolymer mixture of substances of the above-mentioned types, which stem from recovered industrial waste products. Preferably the thermoplastic polymer used as a binder is selected from the group of high density or low density polyethylenes, on account of the comparatively low softening point of such polymers, which temperature is particularly compatible with the limited heat resistance of the leather fibres.

The fibrillar or/and powderous polymeric thermoplastic binder is prepared from the selected thermoplastic polymer by any one of the conventional methods of producing fibrils or/and powder from a polymer. In the fibrillar binder the thermoplastic polymer fibrils have a length generally comprised between 0.1 and 10 millimeters, preferably between 0.5 and 5 millimeters, and a diameter comprised between 0.3 and 100 microns, preferably between 0.5 and 50 microns. When the binder is powderous the particle size of the powder may vary from 60 to 300 microns.

The reinforcing fibres are constituted advantageously by highly resilient textile fibres obtained by spinning or extrusion drawing methods using various polymers, especially polyester, polyamide, polypropylene, poly(vinyl chloride). Prior to being used, these reinforcing fibres may be subjected to a greasing treatment in a manner known *per se* in the art. The reinforcing fibres incorporated in the instant compound material have a length comprised between 5 and 50 millimeters, preferably between 5 and 50 millimeters, preferably between 5 and 20 millimeters, and their denier rating may vary from 1 to 6.

The compound material according to the invention may further include various additives such as pigments, coloring agents, fillers, swelling agents, softeners and, more particularly, feeding oils such as fish oil and neatsfoot oil, and surfactants such as polyvinyl alcohol.

In one advantageous embodiment a portion of the leather fibres incorporated in the compound material is replaced (or substituted) by cellulose fibres. In this embodiment the compound material has a total leather fibre and cellulose fibre content of x%, x having the above-defined value, and the proportion,

by weight, of cellulose fibres may be as high as 40% of the total amount of leather fibres and cellulose fibres, said proportion being preferably comprised between 10 and 35% by weight of the total amount of leather fibres and cellulose fibres.

The compound material according to the invention can be produced in various forms; advantageously it is prepared in the form of sheets or panels. The thickness of said sheets or panels may vary within limits, depending on the particular application envisaged. The thickness may be comprised between several tenths of a millimeter and several tens of millimeters, for instance between 0.5 and 20 millimeters.

The density of the compound material may also vary within wide limits, depending on the particular application envisaged, and is generally comprised between 0.2 and 0.9.

A process or manufacturing a compound material according to the invention comprises:

- a first stage, consisting in thoroughly mixing in an aqueous phase x% by weight of dry matter leather fibres or leather fibres and cellulose fibres, said cellulose fibres representing up to 40%, preferably 10 to 35%, of the total weight of leather fibres and cellulose fibres, y% by weight of dry matter fibrillar or/and powderous polymeric thermoplastic binder, and z% by weight of dry matter reinforcing fibres, x, y and z being so selected than $30 \leq x \leq 80$, $20 \leq y \leq 70$, $5 \leq z \leq 25$, and $x + y + z = 100$, to produce a dispersion, and then producing from said dispersion a moist compound material in the form of a sheet or panel.
- a second stage consisting in drying said moist material at a temperature lower than the degradation temperature of the leather and lower than the softening point of said fibrillary or/and powderous binder, and
- a third stage consisting in subjecting the substantially dry material thus obtained to a heat treatment at a temperature close to the softening point of said binder, while applying to said material at this temperature a controlled pressure for punctually bonding the fibres of said material by a portion of said binder, and for conferring on said compound material a predetermined density.

The first stage of the above novel process comprises thoroughly mixing in an aqueous phase the components of the compound material for obtaining an aqueous dispersion of said components, and then producing a moist compound material in the form of a sheet or panel from said dispersion. The step of mixing said components in an aqueous phase can be carried out by any convenient known method. With a view to obtaining a homogeneous mixture of the components constituting the compound material according to the invention, wettening agents or surfactants adapted to facilitate the dispersion of said components may be added to said aqueous dispersion phase. Possibly used additives, especially coloring agents for coloring the fibres, swelling or expansion agents, fillers, softeners etc. are added to the aqueous phase during the mixing step. The step of producing the moist compound material in the form of a sheet or panel from the aqueous dispersion of the components of said compound material may be carried out in accordance with conventional techniques used in the paper manufacturing field. More particularly, the step of mixing the components of the compound material can be performed in a pulp making machine, and the dispersion thus obtained may be introduced into the head-container (or box) of a paper making machine of the Foudrinier type. The thickness of the moist compound material in the form of a sheet or panel may vary within comparatively wide limits, depending on the particular application envisaged for the final compound material. Thus the thickness may vary, for example, from about 0.5 to about 40 millimeters, and is advantageously comprised between 1 and 20 millimeters. In an advantageous embodiment of the instant novel process, the moist compound material is mildly drained in such a manner that a maximum amount of water is eliminated mechanically, prior to drying, without any deterioration of the organized fibrous structure.

The above-described second stage of the instant novel process consists in drying the moist compound material in the form of a sheet or panel, since after draining, said moist material still contains a considerable proportion of water which may vary from 100% to 200%, by weight, of the dry compound material. The moist material should be dried at a temperature lower than the degradation temperature of the leather, and also lower than the softening point of the fibrillar or/and powderous binder, so as to avoid any hydrothermal degradation of the leather fibres and any premature melting of the fibrillar or/and powderous binder. Advantageously the drying temperature is comprised between 40 and 100°C, a satisfactory drying temperature being comprised between 50 and 60°C. The drying step may be carried out in any conventional continuous controlled-temperature drying device. A hot air tunnel drying device may advantageously be used.

The compound material issuing from the drying step can be handled, but still is comparatively fragile. With a view to subjecting said material to the consecutive treatment steps for producing the final compound material, said material, as issuing from the drying step, may be maintained in the form of a continuous sheet or panel which is treated in a continuous manner, or said material may be cut into separate sheets or panels having a conveient length for discontinuous treatment.

The third stage of the process according to the invention, or thermal bonding stage, consists in subjecting the compound material issuing from the drying step to a treatment step comprising the combined controlled application of heat and pressure with a view to producing punctual bonds between the fibres of the material by means of the fibrillar or/and powderous binder, and to thus producing a final compound exhibiting homogeneous cohesion over its entire thickness, and a selected density.

During this thermal bonding stage, the compound material issuring from the drying stage is first heated to a temperature close to the softening point of the fibrillar or/and powderous binder. Depending on the

nature of said binder, the temperature to which the dried compound material is heated may be comprised between 80°C and 180°C. When using given fibrillar or/and powderous binder, said temperature may advantageously be comprised in the interval defined between a temperature substantially equal to the softening point of the binder and a temperature about 30°C above this softening point. When the polymeric thermoplastic fibrillar or/and powderous binder is a polyethylene binder said heating temperature is advantageously comprised between 100°C and 150°C.

The duration of the heating treatment must be sufficiently long for establishing a homogeneous temperature within the compound material. Depending on the thickness of the material the duration of said treatment may be comprised between 2 and 10 minutes or more.

The heating of the compound material may be carried out by passing said material in the form of a sheet or panel through a conventional oven. Said oven may be provided with conventional gas heating means or with micro-wave heating means, as well as with high-frequency or infra-red heating means.

After the above described heat treatment the compound material is subjected to pressure with a view to obtaining a material having a selected thickness, so as to confer on aid material a homogenous cohesion over its entire thickness, as well as the desired density, which latter may be comprised between 0.2 and 0.9 depending on the particular case envisaged.

The pressing step may be performed by various methods. The material may be pressed, for example, in a discontinuous manner, on a press provided with parallel heating plates and liners; it is also possible to perform continuous pressing by means of a conveniently adjusted heated calender.

The compound material according to the invention can be used for various industrial applications. More particularly, it can be used in the fancy-leather or Morocco-leather industry or in the boot-making industry, especially for manufacturing so-called "first soles" and stiffenings or counters for boots or shoes. Thus, for example, a compound material according to the invention, in the form of a sheet having a density of about 0.6 and a thickness comprised between 1.5 and 2.5 millimeters, exhibits, when used for manufacturing first soles, properties, as far as wear resistance and water absorption and desorption capacity are concerned, which are better than those of the conventional simili-leather materials and the first sole materials based on cellulose fibres.

The compound material according to the invention can also be used for manufacturing filter sheets or cloths, or for manufacturing isolating panels.

The following examples are given with a view to illustrating the invention without limiting the same to the embodiments set forth in said examples.

Example 1

Using a pulp making machine, an aqueous dispersion of a ternary mixture of fibres was prepared, including by weight of dry matter 50% leather fibres having an average length of about 1 millimeter, obtained by dry crushing chrome leather waste, 35% low density polyethylene fibrils obtained by flash-spinning and having an average length of about 1 millimeter and an average diameter of 10 microns, and 15% polyester fibres having a length of about 10 millimeters and a denier rating of 2.7, said polyester fibres being coated or "greased" with polyethylene glycol. Furthermore, 10% by weight neatsfoot oil and 2% by weight acid coloring agent were added to the medium, these two percentages being calculated with reference to the weight of leather fibres; also 0.1% (with respect to the weight of water) non-ionic surfactant was added. The thus obtained dispersion, which contained 5g solid materials in suspension per litre, was stocked in a tub. Said dispersion then was diluted to a concentration of 0.5gr solid matter per litre, and the thus diluted dispersion was introduced into the head box of a paper making machine for producing the compound material in the form of a moist sheet having a thickness of 10 millimeters.

The moist material was then drained under a pressure of 1kg/cm^2, and its thickness after draining was about 6 millimeters. The thus drained material was dried at about 50°C in a hot-air tunnel, then heated in a hot-air tunnel oven at 120°C during 5 minutes, whereafter the material was immediately calendered to a thickness of 2 millimeters.

The thus obtained compound material had a density of about 0.6, and some of its other physico-mechanical properties are listed herein-after:

- Tearing strength 2.5 kg/mm (according to Standard NF G 52 004)
- Tearing-off strength at stich point 6 kg/mm (according to Standard NF G 52-005)
- Bending strength under load 9000 flections
- Water absorption 100-110% (in 8 hours) (according to Standard NF G 52-009)

The compound material prepared by the method described above is particularly adapted to be used in the manufacture of so-called "first soles" for boots, and its properties are improved as compared to those of conventional simili-leather and materials for first soles, which contain mainly cellulose fibres. More particularly the compound material obtained as described hereinbefore has a water-absorption capacity (100-110%) higher than that of conventional simili-leather (80-90%) and that of the cellulose materials (60-70%), and its wet abrasion strength is 2 to 3 times higher than that of conventional simili-leather and cellulose materials.

Example 2

An aqueous suspension of a ternary mixture containing by weight 70% leather waste chips having an average length of about 1 millimeter, 24% low density polyethylene fibrils similar to those used in Example 1, and 6% polypropylene textile fibres having a denier titre of 2.8 and a length of 6 millimeters.

The compound material was formed on a paper making machine, in the shape of a moist sheet

having a thickness of 10 millimeters. This moist compound material was drained and then dried at about 50°C, whereafter it was heated to 125°C and finally calendered to a thickness of 5 millimeters.

The compound material thus obtained was adapted to be used an isolating panels in the building field.

Example 3

Using the same operating conditions as those described in Example 1, a compound material was prepared from a ternary mixture of fibres containing, by weight of dry matter, 45% leather fibres obtained by dry crushing chrome leather and having a length of about 1 millimeter, 40% fibrils obtained by flash-spinning a mixture of olefinic polymers issued from industrial waste recovering, said fibrils having a length of about 1.5 millimeters and a diameter of about 12 microns, and 15% polyamide fibres having a length of about 10 millimeters and a denier titre of 2.5.

The compound material thus obtained exhibited physico-mechanical properties similar to those of the compound material obtained in accordance with Example 1.

Example 4

Applying operating conditions similar to those described in Example 1, a compound material was prepared from a mixture containing, by weight, 35% leather fibres of thekind defined in Example 2, 50% low density polyethylene powder having a particle size comprised between 100 and 200 microns, and 15% greased polyester fibres such as defined in Example 1.

The compound material thus obtained properties comparable to those of the compound material produced in accordance with Example 1.

Example 5

Operating under conditions similar to those described in Example 1, a compound material was prepared from a mixture containing, by weight, 35% leather fibres, 15% bleached cellulose fibres, 32% low density polyethylene fibrils and 18% greased polyester fibres, said leather fibres, polyethylene fibrils and greased polyester fibres being similar to those defined in Example 1.

The thus obtained compound material exhibited physico-mechanical properties similar to those of the compound material produced in accordance with Example 1.

In the foregoing description and the appended claims, the expression "punctual bond" and any expressions derived therefrom are meant to designate a condition wherein the binder does not entirely surround, or coat, the compound material fibres, while a portion of the surface of said fibres is not covered by said binder.

The invention is not limited to the embodiments described above; numerous variants and modifications can be envisaged by those skilled in the art without departing from the spirit and scope of the invention as defined in the appended claims.

CLAIMS

1. A compound material containing leather fibres, reinforcing fibres and a polymeric binder, wherein the fibres are bonded together at points of contact by means of a portion of the polymeric binder, which is a fibrillar or/and powdery thermoplastic polymer having a softening point lower than 180°C, and selected from polyolefins, crystalline copolymers of olefins, crystalline copolymers of olefins and vinyl monomers, mixtures of polyolefins or/and olefin copolymers, polyamides or copolyamides, polyesters, polycarbonates, acrylic polymers, vinyl polymers, and mixtures of said polymers or/and copolymers, said compound material containing by weight x% leather fibres, y% binder and z% reinforcing fibres when $x+y+z=100$, x, y and z being such that $30 \leq x \leq 80$, $20 \leq 7 \leq 70$ and $5 \leq x \leq 25$.

2. A compound material according to claim 1, wherein said leather fibres have a length from 0.2 to 5 millimeters, preferably 0.5 to 3 millimeters.

3. A compound material according to claim 2, wherein said leather fibres are obtained by defibrillating waste leather, by wet refining or by dry crushing.

4. A compound material according to any of claims 1 to 3, wherein the thermoplastic polymer constituting said binder is polyethylene.

5. A compound material according to any of claims 1 to 4, wherein said polymeric thermoplastic binder is of the fibrillar type, the fibrils constituting said fibrillar binder have a length from 0.1 to 10 millimeters, preferably 0.5 to 5 millimeters, and a diameter from 0.3 to 100 microns, preferably 0.5 to 50 microns.

6. A compound material according to any of claims 1 to 4, wherein said polymeric thermoplastic binder is in the form of a powder having a granulometric particle size comprised between 60 to 300 microns.

7. A compound material according to any of claims 1 to 6, wherein said reinforcing fibres have a length from 5 to 50 millimeters, preferably 5 to 20 millimeters, and a denier of 1 to 6.

8. A compound material according to claim 7, wherein said reinforcing fibres are textile fibres selected from polyester, polyamide, polypropylene and poly vinylchloride fibres, said fibres having optionally undergone a sizing treatment.

9. A compound material according to any of claims 1 to 8, further containing additives, such as pigments, coloring agents, fillers, swelling agents, surfactants and/or softening agents.

10. A compound material according to any of claims 1 to 9, further containing cellulose fibres, the total cellulosic and leather fibre content of said material being equal to x%, and the amount of said cellulose fibres representing not more than 40% and being preferably from 10 to 35% of the total weight of cellulose and leather fibres.

11. A compound material according to any of claims 1 to 10, having a density comprised from 0.2 to 0.9.

12. A process of preparing a compound material containing leather fibres, which comprises:

- a first stage consisting in thoroughly mixing in an aqueous phase leather fibres, reinforcing fibres and a polymeric binder, so as to obtain a dispersion of a mixture of said fibres and binder, producing from said dispersion a moist compound material in the form of a sheet or panel,

- a second stage consisting in drying said moist material at a temperature lower than the degradation temperature of the leather and lower than the softening point of said binder, and

- a third phase consisting in subjecting the thus obtained substantially dry compound material to a heat treatment and applying to the heated compound material a pressure to achieve punctual bonding of the fibres of said material by means of a portion of said binder,

- said binder being a fibrillar or/and powderous thermoplastic polymer having a softening point lower than 180°C, said polymer being selected from polyolefins, crystalline olefin copolymers, crystalline copolymers of olefins and vinylic monomers, mixtures of polyolefins or/and olefin copolymers, polyamides or copolyamides, polyesters, polycarbonates, acrylic polymers, vinylic polymers and mixtures of such polymers or/and copolymers,

- said step of thoroughly mixing in an aqueous phase being performed in such a manner that the resulting mixture contains, by weight of dry matter, x% leather fibres a portion of which is possibly replaced by cellulose fibres, y% polymeric thermoplastic binder and z% reinforcing fibres, x, y and z being so selected that $30 \leq x \leq 80$, $20 \leq y \leq 70$ and $5 \leq z \leq 25$, $x+y+z$ being equal to 100, and

- said heat treatment of said substantially dry compound material being performed at a temperature close to the softening point of said binder, while said pressure applied to said material at this temperature is selected so as to confer on said material a predetermined density.

13. A process according to claim 12, wherein the length of said leather fibres is from 0.2 to 5 millimeters, preferably between 0.5 to 3 millimeters, said fibres being obtained by defibrillation of waste leather, preferably by wet refining or dry crushing.

14. A process according to claim 12 or 13, wherein said polymeric thermoplastic binder is a fibrillar binder the fibrils of which have a length from 0.1 to 10 millimeters, preferably 0.5 to 5 millimeters, and a diameter from 0.3 to 100 microns, preferably 0.5 to 50 microns.

15. A process according to claim 12 or 13, wherein said polymeric thermoplastic binder is a powderous binder having a granulometric powder particle size from 60 to 300 microns.

16. A process according to any of claims 12 to 15, wherein said reinforcing fibres have a length comprised between 5 and 50 millimeters, preferably between 5 and 20 millimeters, and a denier titre comprised between 1 and 6, said fibres being preferably textile fibres consisting of a polymer selected from polyesters, polyamides, polypropylene, polyvinyl chloride, said fibres having optionally undergone a greasing treatment.

17. A process according to any of claims 12 to 16, wherein the temperature at which said dried compound material is heated is comprised in an interval defined between a first temperature substantially equal to the softening point of said binder and a second temperature about 30°C higher than said softening point.

18. A process according to any of claims 12 to 16, wherein said fibrillar or/and powderous polymeric thermoplastic binder is a polyethylene, and wherein the temperature to which said dried compound material is heated after said second stage is from 100 to 150°C.

19. A process according to any of claims 12 to 18, wherein the pressure applied to the heated compound material is the pressure built up during a pressure forming process conferring on said material a selected thickness which corresponds to the selected predetermined density, which density is preferably from 0.2 to 0.9.

20. A leather article such as a boot or shoe comprising a material as defined in any of claims 1 to 11.

Printed for Her Majesty's Stationery Office by Croydon Printing Company Limited, Croydon Surrey, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.